Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Information

Sample ID	Nominal Conc. (ng/mL)	Rt (min)	Response	ISTD Response	Response Ratio	Qualifier Ion Ratio	Measured Conc. (ng/mL)	% Recovery
Blank	0	7.01	1155	349755	0.01	11.11	0.00	n/a
	2.5	7.01	15273	362135	0.22	23.28	2.19	87.66
	5	7.01	30868	327071	0.50	19.32	5.05	100.93
	10	7.01	63234	351341	0.97	21.44	9.73	97.29
	17.5	7.01	112678	347010	1.76	20.50	17.64	100.83
	25	7.01	159762	348153	2.50	21.64	24.98	99.93
	37.5	7.01	213301	341990	3.40	21.39	34.00	90.66
	50	7.01	340783	357734	5.20	21.46	51.99	103.98
Blank	0	7.02	724	266901	0.00	37.38	0.03	n/a
	2.5	7.02	11521	268264	0.22	21.26	2.23	89.35
	5	7.02	28950	282669	0.55	24.54	5.49	109.73
	7.5	7.02	54601	298281	0.99	22.47	9.90	98.97
	12.5	7.02	94189	288946	1.77	22.61	17.71	101.22
	25	7.01	141933	296554	2.61	23.70	26.06	104.25
	37.5	7.02	232087	300778	4.21	21.39	42.09	112.24
	50	7.01	284774	307575	5.05	23.32	50.53	101.05

Sample ID	Nominal Conc. (ng/mL)	Rt (min)	Response	ISTD Response	Response Ratio	Qualifier Ion Ratio	Measured Conc. (ng/mL)	% Recovery
Blank	0	2.30	265	238353	0.00	n.a.	0.00	n/a
Curve 1 with ITSD	0.5	2.23	6397	184651	0.03	54.60	0.43	86.40
	1	2.19	13824	204268	0.07	49.20	0.88	88.30
	2.5	2.27	33434	188155	0.18	50.40	2.39	95.40
	5	2.30	74124	230366	0.32	53.30	4.35	87.00
	7.5	2.29	107331	193000	0.56	54.50	7.55	100.70
	12.5	2.29	198558	225211	0.88	48.60	12.00	96.00
	25	2.29	328744	149002	2.21	62.10	31.42	125.70
Blank	0	2.44	675	224755	0.00	n.a.	0.00	n/a

SI Table 1: DPGBE (1/x) weighted regression between 2.5 ng/mL and 50 ng/mL

Sample ID	Nominal Conc. (ng/mL)	Rt (min)	Response	ISTD Response	Response Ratio	Qualifier Ion Ratio	Measured Conc. (ng/mL)	% Recovery
Blank	0	5.43	744	233098	0.00	65.70	0.15	n/a
Curve 1 with ITSD	5	5.43	6955	214846	0.03	104.80	4.83	96.70
	7.5	5.43	9798	212560	0.05	112.50	7.03	93.80
	12.5	5.43	16975	231558	0.07	112.10	12.03	96.20
	25	5.43	35057	221652	0.16	112.00	23.92	95.70
	30	5.43	41436	231846	0.18	119.90	29.62	98.70
	40	5.42	55173	212667	0.26	119.00	37.80	94.50
	50	5.43	69098	149002	0.46	113.60	51.74	103.50
Blank	0	5.43	467	241527	0.00	247.60	0.00	n/a
Curve 2 with ITSD	5	5.43	7007	198860	0.04	123.00	5.29	105.80
	7.5	5.42	10764	206867	0.05	121.80	7.99	106.50
	12.5	5.43	18305	215165	0.09	121.20	13.28	106.30
	25	5.42	33280	206924	0.16	118.80	25.43	101.70
	30	5.42	39608	204573	0.19	124.00	30.69	102.30
	40	5.42	50417	195655	0.26	131.00	40.96	102.40
	50	5.43	61311	197596	0.31	139.90	49.39	98.80

SI Table2: DPGME (1/x) weighted regression between 5.0 ng/mL and 50 ng/mL

Curve 2 with ITSD	0.5	2.29	6887	192204	0.04	46.60	0.45	89.60
	1	2.31	13796	196981	0.07	42.30	0.92	91.50
	2.5	2.28	30826	194290	0.16	48.60	2.13	85.00
	5	2.29	69830	185326	0.38	50.80	5.10	102.10
	7.5	2.28	107117	206736	0.52	48.60	7.03	93.80
	12.5	2.31	189122	213292	0.89	46.60	12.07	96.50
	25	2.27	382093	206511	1.85	47.30	25.22	100.90

SI Table 3: DEGME (1/x) weighted regression between 0.5 ng/mL and 25 ng/mL

	DEGME			DPGBE			DPGME	
Sample ID	Nominal Conc. (ng/mL)	Calc. Conc. (ng/mL)	Sample ID	Nominal Conc. (ng/mL)	Calc. Conc. (ng/mL)	Sample ID	Nominal Conc. (ng/mL)	Calc. Conc. (ng/mL)
QC0.1	0.1	0.093	QC0.5	0.5	0.483	QC1	1	0.953
QC0.1	0.1	0.097	QC0.5	0.5	0.51	QC1	1	0.927
QC0.1	0.1	0.097	QC0.5	0.5	0.484	QC1	1	0.947
QC0.1	0.1	0.102	QC0.5	0.5	0.521	QC1	1	1.031
QC0.1	0.1	0.103	QC0.5	0.5	0.497	QC1	1	0.971
QC0.1	0.1	0.103	QC0.5	0.5	0.471	QC1	1	1.009
QC0.1	0.1	0.097	QC0.5	0.5	0.542	QC1	1	0.992
QC0.1	0.1	0.099	QC0.5	0.5	0.499	QC1	1	1.021
QC0.1	0.1	0.098	QC0.5	0.5	0.525	QC1	1	0.96
QC0.1	0.1	0.099	QC0.5	0.5	0.516	QC1	1	0.913
QC0.1	0.1	0.101	QC0.5	0.5	0.529	QC1	1	0.967
Mean		0.099	Mean		0.507	Mean		0.972
Std Dev		0.003	Std Dev		0.022	Std Dev		0.038
% RSD		3.097	% RSD		4.359	% RSD		3.893
MU		0.006	MU		0.044	MU		0.076
N		11	N		11	N		11

SI Table 4: QC replicates for practical method detection limit assessment for DEGME, DPGBE, and DPGME

	DEGME			DPGBE			DPGME	
Sample ID	Nominal Conc. (ng/mL)	Calc. Conc. (ng/mL)	Sample ID	Nominal Conc. (ng/mL)	Calc. Conc. (ng/mL)	Sample ID	Nominal Conc. (ng/mL)	Calc. Conc. (ng/mL)
BLK	0	0.033	BLK	0	0.0654	BLK	0	0
QC0.5	0.5	0.442	QC2.5	2.5	2.311	QC5	5	4.396
QC0.5	0.5	0.483	QC2.5	2.5	2.347	QC5	5	4.462
QC0.5	0.5	0.451	QC2.5	2.5	2.155	QC5	5	4.503
QC0.5	0.5	0.465	QC2.5	2.5	2.375	QC5	5	4.438
QC0.5	0.5	0.485	QC2.5	2.5	2.261	QC5	5	4.624
QC0.5	0.5	0.446	QC2.5	2.5	2.372	QC5	5	4.625
QC0.5	0.5	0.457	QC2.5	2.5	2.17	QC5	5	4.958
QC0.5	0.5	0.453	QC2.5	2.5	2.418	QC5	5	4.39
QC0.5	0.5	0.451	QC2.5	2.5	2.399	QC5	5	4.738

QC0.5	0.5	0.46	QC2.5	2.5	2.228	QC5	5	4.718
QC0.5	0.5	0.485	QC2.5	2.5	2.162	QC5	5	4.436
Mean		0.462	Mean		2.291	Mean		4.572
Std Dev		0.0159	Std Dev		0.1	Std Dev		0.179
RSD (%)		3.442	RSD (%)		4.365	RSD (%)		3.915
MU		0.0317	MU		0.199	MU		0.358
N		11	N		11	N		11
T95		2.228	T95		2.228	T95		2.228
MDL		0.0353	MDL		0.222	MDL		0.399

SI Table 5: Limit of quantitation QC replicates for DEGME, DPGBE, and DPGME

Optimized Tune Conditions Agilent 6490 LC/MS/MS	
Ion Source	AJS ESI
Ionization Mode	APCI Positive
Mode	MRM
MRM Quantifiers	121.1 m/z → 59.1 m/z
	149.1 m/z → 59.1 m/z
	191.1 m/z → 59.1 m/z
Scan Rate	1.62 spectra/sec
Gas Temperature	250 °C
Vaporizer	350 °C
Gas Flow	14 L/min
Nebulizer	20 psi
Vcapillary	3000 V (+)
Corona Current	4 µA
Fragmentor	380
EMV	400 V (+)
High Pressure RF	150 V
Low Pressure RF	60 V

SI Table 6: Optimized Tune Conditions for an Agilent 6490 LC/MS/MS

Sample ID	Retention Time (min)	ISTD Response	Descriptor	Retention Time (min)	ISTD Response
Initial System Suitability	6.962	221640	Final System Suitability	6.977	183399
	6.959	206957		6.972	189386
	6.956	209279		6.973	194202
	6.959	204158		6.975	193516
	6.956	223085		6.981	178176
Mean	6.958	213024	Mean	6.976	187736
Std Dev	0.003	8730.7	Std Dev	0.004	6858.3
%RSD	0.036	4.098	%RSD	0.051	3.653

SI Table 7: System Suitability for replicate daidzein internal standard injections

Sample ID	Nominal Conc. (ug/L)	Final Conc. (ug/L)	STDEV	%RSD	% Recovery
DEGME QA 1	0.5	0.547	0.008	1.387	109.399
DEGME QA 2	1	1.027	0.046	4.515	102.675
DEGME QA 3	2.5	2.833	0.041	1.438	113.305
DEGME QA4	5	5.748	0.157	2.725	114.956
DEGME QA5	7.5	8.801	0.139	1.578	117.346
DEGME QA6	10	11.714	0.129	1.097	117.145
DEGME QA7	12.5	14.945	0.462	3.089	119.562
DEGME QA8	25	24.973	0.652	2.609	99.890
DPGBE Quality Assurance Samples					
Sample ID	Nominal Conc. (ug/L)	Final Conc. (ug/L)	STDEV	%RSD	% Recovery
DPGBE QA1	1	1.073	0.074	6.895	107.265
DPGBE QA2	7.5	8.676	1.017	11.723	115.678
DPGBE QA3	15	16.355	0.365	2.233	109.035
DPGBE QA4	30	24.269	1.435	5.915	80.896
DPGBE QA5	35	30.611	2.416	7.892	87.459
DPGBE QA6	40	38.420	1.724	4.486	96.050
DPGBE QA7	45	49.910	1.454	2.913	110.911
DPGBE QA8	50	52.586	0.861	1.637	105.172
DPGME Quality Assurance Samples					
Sample ID	Nominal Conc. (ug/L)	Final Conc. (ug/L)	STDEV	%RSD	% Recovery
DPGME QA1	2.5	2.462	0.116	4.714	98.492
DPGME QA2	5	5.592	0.145	2.591	111.835
DPGME QA3	7.5	8.773	0.059	0.678	116.979
DPGME QA4	12.5	14.339	0.103	0.715	114.711
DPGME QA5	30	34.855	0.604	1.732	116.185
DPGME QA6	40	42.715	1.194	2.796	106.787
DPGME QA7	45	45.826	0.694	1.515	101.836
DPGME QA8	50	53.212	1.758	3.304	106.423

SI Table 8: Blind quality assurance samples at various concentrations for DEGME, DPGBE, and DPGME